

## Regeneration of Chrome Etching Solution

Y. van Andel, L.J.J. Janssen

Department of Electrochemical Technology,  
Faculty of Chemical Engineering and Chemistry,  
Eindhoven University of Technology, P.O. box 513,  
5600 MB Eindhoven, the Netherlands

A metal surface is chromitized with a chromic acid solution to obtain a good adherence of polymer coatings on it. In this process Cr(VI) is reduced to Cr(III) and other metals are formed by oxidation of the metal. The oxidation strength of the solution decreases during its use and becomes too low due to a too high Cr(III)/Cr(VI) ratio.

To reduce the chemical waste reduction, the chrome solution needs to be regenerated and purified. Generally the oxidation of Cr(III) to Cr(VI) is carried out with PbO<sub>2</sub> anodes<sup>1,2</sup>. However, this anode material corrodes a little so its use has to be prevented to save the environment. A new anode material, viz. boron-doped diamond, has been proposed to investigate the oxidation of Cr(III) to Cr(VI).

Electrolyses with model and industrial Cr(III) solutions were carried out. Moreover a cost estimation was performed for the generation of a typical chrome bath used in a continuous chromatizing process.

It was found that the current efficiency for Cr(III) oxidation decreases with increasing total current density,  $i_t$ . The current density of Cr(III) oxidation,  $i_{Cr}$ , increases linearly with increasing Cr(III) concentration and is practically independent of the Cr(VI) concentration. Moreover it was found that  $i_{Cr}$  is proportional to  $i_{O_2}^{0.53}$  where  $i_{O_2}$  is the current density of oxygen evolution. From this relation it is concluded that the diffusion of Cr(III) is the rate-determining step for the Cr(III) oxidation at Cr(III) concentrations from 40 to 160 mol m<sup>-3</sup>. The surface of the boron-doped diamond shows no signs of chemical corrosion or mechanical destruction.

A filter-press type cell divided into two compartments by a cation exchange membrane is proposed. A cost calculation was carried out for the oxidation of 1.28 mmol s<sup>-1</sup> Cr(III) in a 40 mol m<sup>-3</sup> chrome solution. It was found that the electrolysis power determines practically completely the total power and that the capital costs for the boron-doped diamond electrodes are about 43 % of the total capital costs. The total costs were calculated at various flow rates of solution. For an industrially acceptable flow rate of 0.5 m s<sup>-1</sup> the minimum total costs are achieved for a plant with 6 cells, where the surface area of each electrode was 0.25 m<sup>2</sup>.

The feasibility of this process is determined strongly by factors like the costs of chemical waste disposal, the costs of chromic acid, government-legislation but to a great extent the costs of the new anode material.

### References:

1. D. Pletcher and F.C. Walsh, *Industrial Electrochemistry*, Blackie Academic & Professional, 367 (1982)
2. D. Genders and N. Weinberg (editors), *Electrochemistry for a cleaner environment*, Electrosynthesis Company Inc., 366 (1992)

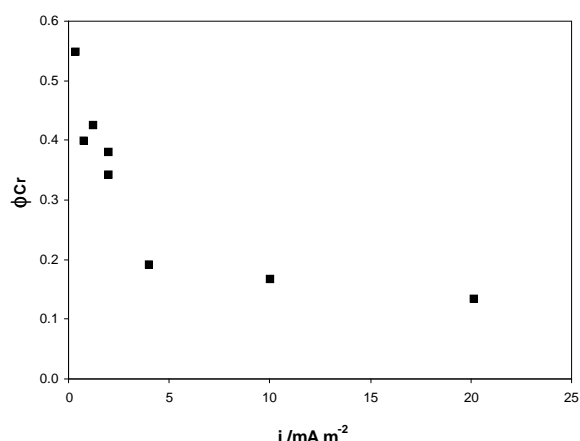


Fig. 1. Current efficiencies of chrome(III) oxidation for industrial Cr(III) solution with boron-doped diamond electrode sheet of 0.248 cm<sup>2</sup> placed vertically in solution at 25 °C

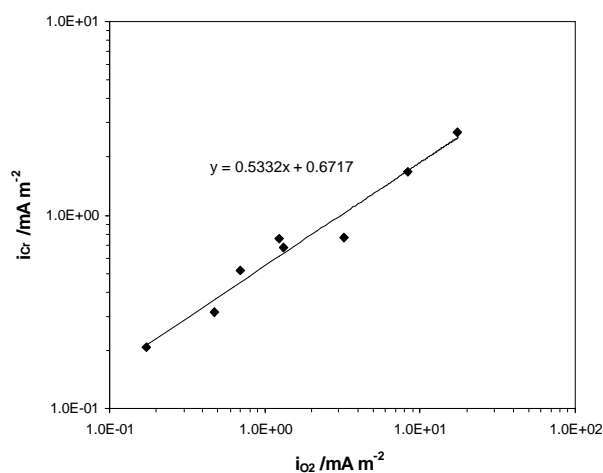


Fig. 2.  $i_{Cr}$  as a function of  $i_{O_2}$  on a double logarithmic scale for industrial Cr(III) solution with boron-doped diamond electrode sheet of 0.248 cm<sup>2</sup> placed vertically in solution at 25 °C

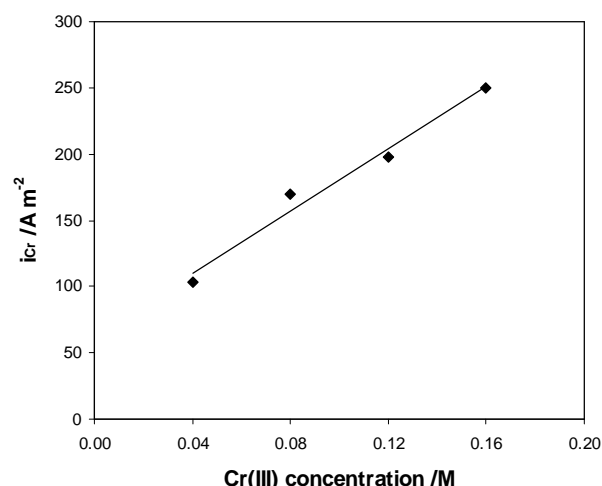


Fig. 3.  $i_{Cr}$  versus Cr(III) concentration at  $i_{O_2} = 800 \text{ A/m}^2$  on a vertically placed boron-doped diamond electrode (0.195 cm<sup>2</sup>) in model solutions with 0.2 M Cr(VI), 0.1 M HNO<sub>3</sub> and varying Cr(III) concentrations at 25 °C